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(54) Title: OXIDATION OF ALKYL-AROMATIC COMPOUNDS

(57) Abstract: A process for the oxidation of an alkyl-aromatic compound, wherein the aromatic compound is admixed with an oxidising agent or sulfur compound in the presence of an ionic liquid is described. In this process, air, dioxygen, peroxide, superoxide, any other form of active oxygen, nitrite, nitrate, nitric acid or other oxides (or oxyhalides) of nitrogen (hydrate or anhydrous) are preferably used as the oxidising agent. The process is usually under Bronsted acidic conditions. The product of the oxidation reaction is preferably a carboxylic acid or ketone or an intermediate compound in the oxidation such as an aldehyde, or alcohol. The oxidation is preferably performed in an ionic liquid containing an acid promoter such as methanesulfonic acid.

**BEST AVAILABLE COPY**

1  
2  
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5  
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9  
10 Oxidation of alkyl-aromatic compounds  
11

12 This invention relates to a process for the oxidation  
13 of aromatic compounds such as toluene and xylene. The  
14 oxidation of compounds such as toluene and xylene are  
15 important reactions and are carried out on a large  
16 scale. The products of the oxidation reactions, e.g.  
17 terephthalic acid, are widely used in the polymer  
18 industry.  
19

20 Various methods exist for the oxidation of toluene,  
21 including oxidation with dioxygen, using a  
22 cobalt(III)<sup>1,2</sup> catalyst, periodate,<sup>3</sup> air using  
23  $\text{Cs}_5[\text{SiW}_{11}\text{O}_{39}\text{Ru(III)(H}_2\text{O)}] \cdot 7 \text{ H}_2\text{O}$  as a catalyst (59%  
24 yield),<sup>4</sup> hypochlorite catalysed by Ru(VIII)oxide  
25 tetroxide in  $[\text{Bu}_4\text{N}]\text{Br}$ .<sup>5</sup> These methods work well, but  
26 require either stoichiometric quantities of oxidising  
27 agent or require special catalysts.  
28

29 We have developed a procedure for the oxidation of<sup>2</sup>  
30 alkylated aromatic compounds that either partially or  
31 completely oxidises the alkyl group to an alcohol,  
32 aldehyde, ketone or carboxylic acid.

CONFIRMATION COPY

1  
2 Thus, according to one aspect of the present invention,  
3 there is provided a process for the oxidation of an  
4 alkyl-aromatic compound, wherein the aromatic compound  
5 is admixed with an oxidising agent or sulfur compound  
6 in the presence of an ionic liquid.

7  
8 In this process, air, dioxygen, peroxide, superoxide,  
9 any other form of active oxygen, nitrite, nitrate,  
10 nitric acid or other oxides (or oxyhalides) of nitrogen  
11 (hydrated or anhydrous) are preferably used as the  
12 oxidising agent. The process is usually under Bronsted  
13 acidic conditions.

14  
15 Preferably, the process involves the oxidation of the  
16 alkyl side chain of the aromatic compound in the  
17 presence of a nitrogen oxyacid species such as nitrate  
18 or nitric acid. This nitrogen(V) species oxidises the  
19 alkyl group, and is in turn reduced to a lower valent  
20 form of nitrogen. This lower valent form of nitrogen  
21 can be re-oxidised back to nitrogen(V) by means of an  
22 oxidising agent. Other oxidising agents suitable  
23 include dioxygen (air), oxygen, peroxides, superoxides.

24  
25 Other suitable oxidating agents are certain sulfur  
26 compounds such as the sulfur acid/bases, eg  $\text{H}_2\text{SO}_4$  or  
27  $\text{H}_2\text{SO}_3$ .

28  
29 This invention also allows for the separation of the  
30 ionic liquid and product by physical or chemical means  
31 such as distillation, steam distillation, azeotropic  
32 distillation, sublimation, gravity separation, solvent

1 extraction, crystallisation, supercritical fluid  
2 extraction and chromatography.

3  
4 Ionic liquids consist of two components, which are a  
5 positively charged cation and a negatively charged  
6 anion. Generally, any compound that meets the  
7 criterion of being a salt (consisting of an anion and  
8 cation) and is fluid at or near the reaction  
9 temperature or exists in a fluid state during any stage  
10 of the reaction may be defined as an ionic liquid.

11  
12 The cation for the present process is preferably a 1,  
13 3-dialkylimidazolium cation such as 1-methyl-3-  
14 butylimidazolium. Other cations for this process are  
15 ammonium, pyrazolium, and other pyridinium, alkyl- or  
16 poly-alkylpyridinium, alkyl- or poly-alkyl phosphonium  
17 cations.

18  
19 The anion for the process is preferably a sulfur-  
20 containing anion, such as sulfate, hydrogensulfate.  
21 Non-sulfur containing anions include those based on  
22 nitrogen, phosphorus, boron, silicon, selenium,  
23 tellurium, halogens, oxoanions of metals, and organic  
24 anions, such as trifluoroacetate, acetate, and anions  
25 that are arsenic, antimony, and bismuth based. The  
26 preferred anions are nitrate or methanesulfonate.

27  
28 More than one ionic liquid or any combination of ionic  
29 liquids can be used in the present invention.  
30 Suitable Process conditions.

31 Temperature: ideally 100-120°C but to include 0° to  
32 250°C

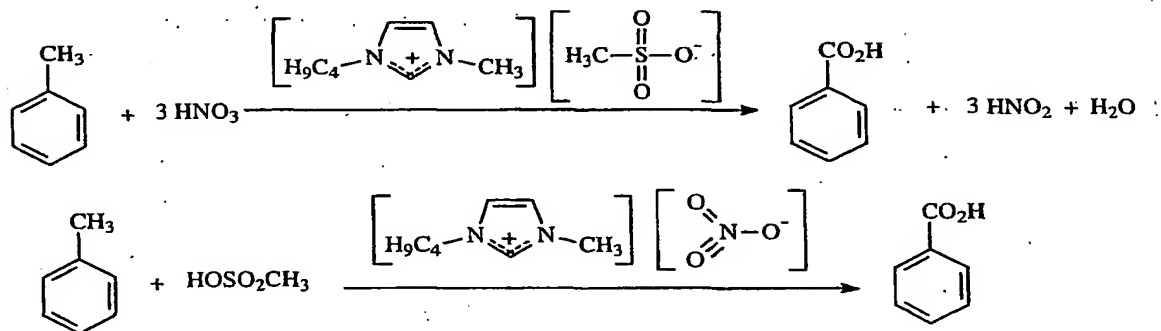
1 Pressure: ideally, atmospheric, but include 1 mbar  
 2 to 100 bar  
 3 Time: ideally 24-48 hours, can be 1 minute to  
 4 1 month.

5  
 6 The reaction preferably requires an acid to be present.  
 7 This acid is generally an oxoacid of nitrogen, sulfur,  
 8 selenium, tellurium, phosphorus, arsenic, antimony, or  
 9 an organic acid anion (e.g. acetate, trifluoroacetate).

10

11 The oxidation of toluene is shown in scheme.1. As can  
 12 be seen, the reaction can be carried out in [bmim][OMs]  
 13 ("OMs" = methanesulfonate) by the addition of nitric  
 14 acid or in [bmim][NO<sub>3</sub>] by the addition of  
 15 methanesulfonic acid.

16



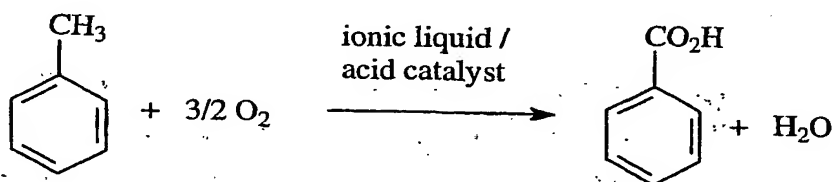
20 Scheme 1. The oxidation of toluene to benzoic acid.

21

22 As the reaction proceeds, the nitrate or nitric acid  
 23 (the oxidising agent) is believed to be reduced to  
 24 nitrous acid, which is  
 25 unstable under the acidic conditions employed in the  
 26 reaction. This in turn is re-oxidised back to  
 27 nitrate/nitric acid by an oxidising agent. The

1 dioxygen in air will suffice, but other oxidants such  
2 as peroxides are also suitable.

3  
4 The reaction can be carried out using a stoichiometric  
5 amount of nitric acid (or nitrate) or can be performed  
6 catalytically. In the latter case, if air is used to  
7 re-oxidise the nitrous acid formed in the reaction, the  
8 overall reaction is shown in scheme 2.



12  
13 Scheme 2: The overall reaction for the oxidation of  
14 toluene in air.

15  
16 Other compounds oxidizable by this invention are o- or  
17 p-xylene, firstly to o- or p-toluic acid (2- or 4-  
18 methylbenzoic acid) then to phthalic acid or  
19 terphthalic acids respectively. Ethylbenzene and n-  
20 propylbenzene can be oxidized under similar conditions  
21 to acetophenone and propiophenone as the major  
22 products. Also formed in these two reactions are  
23 benzoic acid, presumably from oxidative cleavage of the  
24 alkyl group.

25  
26 The present invention is further illustrated with  
27 reference to the following Examples:

1

2 Examples:

3

4 1. Oxidation of toluene in [bmim][OMs]

5 In a round-bottomed flask (25cm<sup>3</sup>) equipped with a  
6 magnetic stirrer flea and reflux condenser, 1-butyl-  
7 3-methylimidazolium methanesulfonate (0.23g, 1 mmol)  
8 and toluene (0.18g, 2 mmol) were added. 67% aqueous  
9 nitric acid (0.28g, 3 mmol) was cautiously added and  
10 the mixture heated under reflux for 48 hours. The  
11 flask was cooled and the products analysed by gas  
12 chromatography. All of the toluene had reacted and  
13 signals due to benzoic acid (70 % yield) and a by-  
14 product (2- and 4-nitrotoluene) were detected. The  
15 product(s) was isolated by Kugelrohr distillation at  
16 5 mm Hg. This gave pale yellow oil (bp = 100°C at 5  
17 mmHg) nitrotoluene and a colourless solid (bp = 150°C  
18 at 5 mmHg) - benzoic acid. The structures were  
19 confirmed by NMR analysis and were in accordance  
20 with authentic material.

21

22

23 2. Oxidation of toluene in [bmim][OMs]

24 In a round-bottomed flask (25cm<sup>3</sup>) equipped with a  
25 magnetic stirrer flea and reflux condensed, 1-butyl-  
26 3-methylimidazolium methanesulfonate (0.23g, 1 mmol)  
27 and toluene (0.46g, 5 mmol) were added. 67% aqueous  
28 nitric acid (0.18g, 2 mmol) was cautiously added and  
29 the mixture heated under reflux for 48 hours. The  
30 flask was cooled and the products analysed by gas  
31 chromatography. All of the toluene had reacted and  
32 signals due to benzoic acid (90% yield) and a by-

1 product (2- and 4-nitrotoluene) were detected. The  
2 product(s) was isolated by Kugelrohr distillation at  
3 5 mmHg. This gave pale yellow oil (bp = 100°C at 5  
4 mmHg) nitrotoluene and a colourless solid (bp = 150°  
5 at 5 mmHg) - benzoic acid. The structures were  
6 confirmed by NMR analysis and were in accordance  
7 with authentic material.

8

9 3. Oxidation of toluene in [bmim][NO<sub>3</sub>]

10 In a round-bottomed flask (25cm<sup>3</sup>) equipped with a  
11 magnetic stirrer flea and reflux condensed, 1-butyl-  
12 3-methylimidazolium nitrate (0.23g, 2 mmol) and  
13 toluene (0.46g, 5 mmol) were added. 67%  
14 methanesulfonic acid (0.29g, 3 mmol) was cautiously  
15 added and the mixture heated under reflux for 48  
16 hours. The flask was cooled and the products  
17 analysed by gas chromatography. All of the toluene  
18 had reacted and signals due to benzoic acid (85%  
19 yield) and a by-product (2- and 4-nitrotoluene) were  
20 detected. The product(s) was isolated by Kugelrohr  
21 distillation at 5 mmHg. This gave pale yellow oil  
22 (bp = 100°C at 5 mmHg) nitrotoluene and a colourless  
23 solid (bp = 150° at 5 mmHg) - benzoic acid. The  
24 structures were confirmed by NMR analysis and were  
25 in accordance with authentic material.

26

27 4. Oxidation of ethylbenzene

28 In a 50 cm<sup>3</sup> round bottomed flask, equipped with a  
29 magnetic stirrer and reflux condenser, was added  
30 ethylbenzene (1.06 g, 10 mmol) and [bmim][OMs] (1.0  
31 g). 67 % Nitric acid (0.45 g, 5 mmol) was  
32 cautiously added and the mixture heated under



1 reflux. After 48 hours the mixture was analysed by  
2 gas chromatography and found to contain 19 %  
3 unreacted ethylbenzene, 23 % benzoic acid and 57 %  
4 acetophenone. The mixture was cooled and water (50  
5 cm<sup>3</sup>) was added. The products were extracted with  
6 diethyl ether (4 x 20 cm<sup>3</sup>), concentrated on a rotary  
7 evaporator and purified by Kugelrohr distillation.  
8 This gave acetophenone (0.62 g, 51 %) and benzoic  
9 acid (0.22 g, 18 %).

10

11 5. Oxidation of *p*-xylene

12 In a 50 cm<sup>3</sup> round bottomed flask, equipped with a  
13 magnetic stirrer and reflux condenser, was added *p*-  
14 xylene (1.07 g, 10 mmol) and [bmim][OMs] (2.0 g).  
15 67 % Nitric acid (0.90 g, 10 mmol) was cautiously  
16 added and the mixture heated under reflux. After 24  
17 hours the mixture was analysed by gas chromatography  
18 (approximately 50 % conversion), cooled and water  
19 (50 cm<sup>3</sup>) was added. The resultant precipitate was  
20 collected by filtration and purified by vacuum  
21 sublimation on a Kugelrohr apparatus. This gave two  
22 crystalline solids, that were identified as 4-  
23 methylbenzoic acid (0.50 g, 37 %) and benzene-1,4-  
24 dioic acid (terephthalic acid) (0.08 g, 5 %). The  
25 remainder was unreacted *p*-xylene.

26

27 The aqueous filtrate containing the ionic liquid was  
28 concentrated on a rotary evaporator (80°C at 50  
29 mmHg) and transferred to the 50 cm<sup>3</sup> round bottomed  
30 flask, equipped with a magnetic stirrer and reflux  
31 condenser. *p*-Xylene (5.35g, 50 mmol) and 67% nitric  
32 acid (0.90 g, 10 mmol) was added. The mixture was

1 heated under reflux for 5 days, then cooled to room  
2 temperature. During this time some of the *p*-xylene  
3 was lost through evaporation. Dilution with water,  
4 filtration and sublimation (as above) gave 4-  
5 methylbenzoic acid (1.63 g, 24 %) and benzene-1,4-  
6 dioic acid (terephthalic acid) (0.24 g, 3 %). The  
7 remainder was unreacted *p*-xylene.

8

9 6. Oxidation of *o*-xylene

10 In a 50 cm<sup>3</sup> round bottomed flask, equipped with a  
11 magnetic stirrer and reflux condenser, was added *o*-  
12 xylene (1.07 g, 10 mmol) and [bmim][OMs] (1.0 g).  
13 67 % Nitric acid (0.45 g, 5 mmol) was cautiously  
14 added and the mixture heated under reflux. After 40  
15 hours the mixture was analysed by gas chromatography  
16 and gave 42 % conversion to 2-methylbenzoic acid and  
17 trace of phthalic acid. The remainder was unreacted  
18 *o*-xylene.

19

20

21 7. Oxidation of propylbenzene

22

23 In a 50 cm<sup>3</sup> round bottomed flask, equipped with a  
24 magnetic stirrer and reflux condenser, was added  
25 propylbenzene (1.21 g, 10 mmol) and [bmim][OMs] (1.0  
26 g). 67 % Nitric acid (0.45 g, 5 mmol) was  
27 cautiously added and the mixture heated under  
28 reflux. After 54, 80 hours the mixture was analysed  
29 by gas chromatography and found to give 15 %  
30 conversion. Three products were identified (GCMS)  
31 as: propiophenone, benzoic acid and 3-phenylpentane  
32 in the ratio (2 : 1 : trace).

1 In particular, the present invention relates to a  
2 process whereby aromatic compounds bearing an alkyl  
3 substituent are oxidised on the alkyl chain on the  
4 carbon atom next to the aromatic ring, and where the  
5 oxidation is performed in an ionic liquid.

6  
7 The product of the oxidation reaction is preferably  
8 a carboxylic acid or ketone or an intermediate  
9 compound in the oxidation such as an aldehyde, or  
10 alcohol.

11  
12 The oxidation is preferably performed in an ionic  
13 liquid containing an acid promoter such as  
14 methanesulfonic acid.

15  
16 The oxidation is preferably performed in an ionic  
17 liquid containing a nitrogen acid or salt such as  
18 nitric acid, nitrous acid, nitrate or nitrite salt.  
19 The ionic liquid/acidic promoter combination can be  
20 used as a catalyst for the oxidation.

21  
22 The ionic liquid/acidic promoter can be re-oxidised  
23 by an oxidising agent (such as dioxygen in air), and  
24 the ionic liquid/acidic promoter can be recycled and  
25 reused in further reactions.

26  
27 The ionic liquid/acidic promoter can be separated  
28 from the product by some physical or chemical means  
29 such as distillation, steam distillation, azeotropic  
30 distillation, sublimation, gravity separation,  
31 solvent extraction, crystallisation, supercritical  
32 fluid extraction and chromatography.

1

2 The present invention also extends to the use of an  
3 ionic liquid in the oxidation of an alkyl-aromatic  
4 compound, as well as an oxidised alkyl-aromatic  
5 compound whenever prepared by a process of the  
6 present invention.

7

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9

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18

1     Claims

2

3     1.    A process for the oxidation of an alkyl-  
4           aromatic compound, wherein the aromatic  
5           compound is admixed with an oxidising agent or  
6           sulfur compound in the presence of an ionic  
7           liquid.

8

9     2.    A process as claimed in Claim 1 wherein the  
10          oxidising agent is one or more of the group  
11          comprising: air, dioxygen, peroxide,  
12          superoxide, any other form of active oxygen,  
13          nitrite, nitrate, nitric acid or other oxides  
14          (or oxyhalides) of nitrogen (hydrated or  
15          anhydrous) and sulfur acid/bases such as  
16          sulfuric acid or sulfonic acid.

17

18     3.    A process as claimed in Claim 1 or Claim 2  
19          wherein the process is carried out under  
20          Bronsted acidic conditions.

21

22     4.    A process as claimed in any one of the  
23          preceding Claims involving the oxidation of the  
24          alkyl sidechain of the aromatic compound in the  
25          presence of a nitrogen oxyacid species.

26

27     5.    A process as claimed in Claim 4 wherein the  
28          nitrogen oxyacid species is a nitrate or nitric  
29          acid.

30

31     6.    A process as claimed in any one of the  
32          preceding Claims wherein the ionic liquid and

1 reaction products can be separated by means of  
2 one or more of the following processes  
3 comprising: distillation, steam distillation,  
4 azeotropic distillation, sublimation, gravity  
5 separation, solvent extraction,  
6 crystallisation, supercritical fluid extraction  
7 and chromatography.  
8

9 7. A process as claimed in any one of the  
10 preceding Claims wherein the cation of the  
11 ionic liquid is one or more of the group  
12 comprising: ammonium, pyrazolium, 1,3-  
13 dialkylimidazolium, pyridinium, alkyl- or poly-  
14 alkylpyridinium, alkyl- or poly-alkyl  
15 phosphonium.  
16

17 8. A process as claimed in Claim 7 wherein cation  
18 is a 1, 3-dialkylimidazolium cation such as 1-  
19 methyl-3-butyylimidazolium.  
20

21 9. A process as claimed in any one of the  
22 preceding Claims wherein the anion of the ionic  
23 liquid is one or more of the group comprising:  
24 a sulfur-containing anion, such as sulfate,  
25 hydrogensulfate, non-sulfur-containing anions  
26 including those based on nitrogen, phosphorus,  
27 boron, silicon, selenium, tellurium, halogens,  
28 oxoanions of metals, and organic anions, such  
29 as trifluoroacetate, acetate, and anions that  
30 are arsenic, antimony, and bismuth-based.  
31

- 1     10. A process as claimed in Claim 9 wherein the  
2         anion is nitrate or methanesulfonate.  
3
- 4     11. A process as claimed in any one of the  
5         preceding Claims wherein more than one ionic  
6         liquid or any combination of ionic liquids is  
7         used.  
8
- 9     12. A process as claimed in any one of the  
10        preceding Claims wherein an acid is present.  
11
- 12    13. A process as claimed in Claim 12 wherein the  
13        acid is one or more of the group comprising: an  
14        oxoacid of nitrogen, sulfur, selenium,  
15        tellurium, phosphorus, arsenic, antimony, or an  
16        organic acid anion (e.g. acetate or  
17        trifluoroacetate).  
18
- 19    14. A process as claimed in claim 13 wherein the  
20        acid is one or more of the following group  
21        comprising: methanesulfonic acid, nitric acid,  
22        nitrous acid, nitrate or a nitrate salt.  
23
- 24    15. A process as claimed in any one of Claims 12 to  
25        14 wherein the ionic liquid/acid combination  
26        also acts as a catalyst for the oxidation.  
27
- 28    16. A process as claimed in any one of Claims 12 to  
29        15 wherein the acid can be re-oxidised by an  
30        oxidising agent such as dioxygen in air.  
31

- 1 17. A process as claimed in any one the preceding  
2 Claims wherein the ionic liquid is [bmin] [OMs]  
3 and the oxidising agent is nitric acid.  
4
- 5 18. A process as claimed in any one of Claims 1 to  
6 16 wherein the ionic liquid is [bmin] [NO<sub>3</sub>] and  
7 the oxidising agent is methanesulfonic acid.  
8
- 9 19. A process as claimed in any one of the  
10 preceding Claims for the oxidation of  
11 alkylaromatics, toluene, xylene, or a benzene.  
12
- 13 20. A process as claimed in Claim 19 for the  
14 oxidation of p-xylene.  
15
- 16 21. A process as claimed in any one of the  
17 preceding Claims wherein the alkyl chain on the  
18 carbon atom next to the aromatic ring is  
19 oxidised.  
20
- 21 22. A process as claimed in any one of the  
22 preceding Claims for the preparation of an  
23 aldehyde or alcohol.  
24
- 25 23. Use of an ionic liquid in a process as claimed  
26 in any one of Claims 1 to 22.  
27
- 28 24. Use of an ionic liquid in the oxidation of  
29 alkylaromatics, toluene, xylene or a benzene.  
30



- 1        25.    An oxidated alkyl-aromatic compound obtainable  
2            by a process as defined in any one of Claims 1  
3            to 22.  
4
- 5        26.    A compound as claimed in Claim 25 wherein the  
6            alkyl aromatic starting compound is an  
7            alkylaromatic, toluene, xylene or a benzene.  
8
- 9        27.    A process substantially as hereindescribed and  
10        with reference to the Examples.

## INTERNATIONAL SEARCH REPORT

Int ional Application No

PCT/GB 01/04426

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07C51/265

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 199 01 524 A (WAFFENSCHMIDT HORST ; KEIM WILHELM (DE); WASSERSCHIED PETER (DE)) 20 July 2000 (2000-07-20) example 5	1-27
X	WO 00 32572 A (MURPHY VINCE ; HAGEMEYER ALFRED (US); POOJARY DAMODARA M (US); SYM) 8 June 2000 (2000-06-08) page 25, line 16,26	1-27

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

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